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ULTRASONIC ABSORPTION IN SOLUTIONS

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(*Received for publication, October, 20, 1954,*
Received after revision, March, 31, 1955)

ABSTRACT. Equations have been derived for the excess ultrasonic absorption in solutions due to occurrence of chemical reaction accompanied by a change of volume. Modifications for aqueous solutions of electrolytes have been worked out. The results explain some of the anomalous values of sound absorption in bivalent sulphate solutions.

Freedman (1953) has derived equations for ultrasonic absorption and relaxation frequency due to relaxing specific heat of chemical reaction. His theory is remarkably successful for acetic and propionic acids. Freedman assumes no change in volume; most chemical reactions are, however, accompanied by both changes of volume and temperature. If change of volume ΔV, alone, in a chemically reacting solution with n_i moles of the ith species, is taken into consideration, we can analogously deduce, that the reaction compressibility is

$$\beta_0^{\tau *} = \frac{(\Delta V)^2}{VRT} \cdot \frac{D}{1+i\omega\frac{D}{U}} = \frac{\beta_0^{\tau}}{1+i\omega\tau}$$

where $\beta_0^{\tau} = \frac{D(\Delta V)^2}{VRT}$; $D = \left[\sum \frac{a_i^2}{n_i} - \frac{(\Sigma a_i^2)^2}{n_i} \right]^{-1}$;

a_i is the stoichiometric coefficient of the ith reaction component;

U is the gross reaction rate an $d\tau = \frac{D}{U}$ is the time lag.

Writing the effective compressibility as

$$\beta_0^0 = \beta_0^{\infty} + \frac{\beta_0^{\tau}}{1+i\omega\tau}$$

we can deduce by well known methods that for a frequency ν, the absorption coefficient per cm. is given by

$$\frac{\alpha}{\nu^2} = 2\pi^2 v\rho \frac{\beta_0^{\tau}\tau}{1+\omega^2\tau^2}$$ where v is the velocity

so that the relaxation frequency is

$$\nu_m = \frac{1}{2\pi\tau} = \frac{1}{2\pi}\frac{U}{D}$$

and the intensity absorption per wavelength

$$\mu = 2\alpha\lambda = 2\pi\rho v^2\beta_0^r \frac{\omega\tau}{1+\omega^2\tau^2}$$

μ has therefore a maximum for $\omega\tau = 1$, the maximum value being given by

$$\mu_m = \pi\rho v^2\beta_0^r = \pi\rho \frac{D(\Delta V)^2}{VRT}$$

In a first order reaction < like $A \rightleftharpoons A^*$ or $A \rightleftharpoons B$ it can be easily shown that

$$\mu_m = \frac{\pi}{V}\frac{(\Delta V)^2}{\beta_0^0 RT}\alpha(1-\alpha)$$

where α is the degree of formation of A^* or B.

For a second order reaction like $AB \rightleftharpoons A+B$

$$\mu_m = \frac{\pi}{V}\frac{(\Delta V)^2}{\beta_0^0 RT}\frac{\alpha}{2}(1-\alpha^2.)$$

The above theory assumes an ideal solution where the components exist in their pure phases. To apply thermodynamics to solutions of electrolytes, for example, the activity must be considered. Activity will determine the rate and rate constants. Further, in most chemical reactions of physicochemical interest,the solvent is in such great excess, that its concentration does not change appreciably as the reaction proceeds to completion.

Writing the equilibrium constant as

$$K = \Pi(n_i f_i)^{ai}$$

f_i denoting the activity coefficient of i th component, we use the thermodynamic relationship

$$\frac{\partial}{\partial p}\log K = -\frac{\Delta V^0}{RT}$$

where ΔV^0 is the change in molar volume referred to a standard state.

But $$\frac{\partial}{\partial p}\log K = \sum \frac{a_i}{n_i}\frac{\partial n_i}{\partial p} + \sum \frac{a_i}{f_i}\frac{\partial f_i}{\partial p}$$

We can always write f_i as a function of n_i, so that

$$\delta f_i = \frac{\partial f_i}{\partial n_i}\delta n_i$$

$$\therefore \quad \frac{\partial}{\partial p}\log K = \left[\sum \frac{a_i^2}{n_i} + \sum \frac{a_i^2}{f_i}\frac{\partial f_i}{\partial n_i}\right]\frac{\partial Z}{\partial p} = \frac{1}{D^*}\frac{\partial Z}{\partial p}$$

where $\delta n_i = a_i \delta Z$

and $$D^* = \left[\sum \frac{a_i^2}{n_i} + \sum \frac{a_i^2}{f_i}\frac{\partial f_i}{\partial n_i}\right]^{-1}$$

so that $$\beta_0^* = \frac{D^*(\Delta V^0)^2}{VRT}$$

The gross reaction rates can be written as

$$U_f = k_f \pi (n_i f_i)^{-a_i} \qquad a_i < 0$$

$$U_b = k_b \pi (n_i f_i)^{+a_j} \qquad a_j > 0$$

and the dynamic compressibility can be deduced to be

$$\beta_0^* = \frac{(\Delta V^0)^2}{VRT}\,\frac{D^*}{1+i\omega D^*/U} = \frac{\beta_0^*}{1+i\omega\tau}$$

where $$\tau = \frac{D^*}{U}$$

giving $$\mu_m = \frac{\pi}{V}\,\frac{D^*(\Delta V^0)^2}{\beta_0^* RT}$$

where V is the total volume of the solution. Thus absorption will depend on both degree of dissociation and activity coefficients. Both should be known and also the nature of variation of activity coefficient with concentration.

1-1 electrolytes, like NaCl and KBr etc., are very nearly cent per cent dissociated and their activity coefficients approximate unity. So dissociation reaction has negligible contribution to ultrasonic absorption. The negative absorption (less than water) observed in higher concentrations of these salts is due to the depolymerising effect on water; the three bonded structure becoming less and less numerous with increase of concentration.

Of great theoretical interest is the excess absorption in bivalent sulphates in the low frequency region. Absorption per wavelength gives two clear maxima in some sulphates, one in the 1-10 megacycle range and another in 100 megacycle range. The values of μ_m are strictly proportional to concentration and ν_m is independent of concentration in the range 0.01 to 0.1 M. Concentration-independance of the relaxation frequency indicates at the outset a first order reaction. If c is the concentration of the electrolyte in moles per litre and α the degree of dissociation or hydration; $D^* = D = \alpha(1-\alpha)c$

$$\frac{\mu_m}{c} \qquad \frac{\pi}{1000}\,\frac{(\Delta V)^2}{\beta_0 RT}\,\alpha(1-\alpha)$$

Taking a minimum volume change of 20 c.c. the value of α should be very nearly one to explain the experimental results.

From recent experiments (1952) it has been found that the degree of dissociation of bivalent sulphates is nearly constant in the same concentration range and is due to the activity coefficients being inversely proportional to the square root of concentration.

$$f_i \propto \frac{1}{\sqrt{c_i}} \quad \therefore \quad \frac{1}{f_i}\frac{\partial f_i}{\partial n_i} = -\frac{1}{2\alpha c} \quad \text{for ions}$$

and $$\frac{1}{f_i}\frac{\partial f_i}{\partial n_i} = 0 \quad \text{for undissociated molecules}$$

whence $$\frac{\mu_m}{c} = \frac{\pi}{1000}\frac{(\Delta V^0)^2}{\beta^0 RT}\cdot \alpha(1-\alpha)$$

So $\frac{\mu_m}{c}$ is expected to be constant so long as α is constant. Further

$$U_f = k_f.(\alpha c).(\alpha c)\, f_{R^{++}} \times f_{so_4} = \text{const.}\, k_f\, \alpha^2 c$$

and $$U_b = k_b\,(1-\alpha)c$$

If α is constant, at equilibrium, the net gross reaction rate U is proportional to the concentration. Since

$$\nu_m = \frac{1}{2\pi}\frac{U}{D^*} = \frac{1}{2\pi}\frac{U}{\alpha(1-\alpha)c}$$

ν_m is also independent of concentration.

Although the dissociation reaction $RSO_4 \rightleftharpoons R^{++}+SO_4^{--}$ explains the results qualitatively, the quantitative agreement is poor. Taking the experimental value $\alpha = 0.9$ for, say, $MgSO_4$, we must take $(\Delta V^0)_1 = 5$ c.c. and $(\Delta V^0)_2 = 10$ c.c. to explain the two maxima. In any case, the high degree of dissociation of sulphates does not indicate such a low value of ΔV^0.

The only plausible and satisfactory picture is to consider a mechanism of the type

$$\begin{array}{l} RSO_4 \rightleftharpoons R^{++}+SO_4^{--} \\ \quad\downarrow\uparrow \\ \text{ion pair } [R^{++}SO_4^{--}] \\ \quad\downarrow\uparrow \\ R^{++}+SO_4 \end{array}$$

The undissociated RSO_4 is in simultaneous equilibrium with a biwise dissociation reaction, some of it directly dissociating to bivalent ions, while others break their electronic linkages forming the so called ion pairs of Bjerrum, which further dissociate to the ions. If the net measured concentration of each ion be αc and if α' be the degree of formation of the ion pair, then the

concentration of undissociated molecules is $(1-\alpha)(1-\alpha')c$ and of pair $\alpha'(1-\alpha)c$. However, for explaining the values of activation energies the total step

$$RSO_4 \rightleftharpoons [R^{++}SO_4^{--}] \rightleftharpoons R^{++} + SO_4^{--}$$

may be taken to be responsible for the absorption of the lower maximum. Of these the step $RSO_4 \rightleftharpoons (R^{++}SO_4^{--}]$ is associated with a considrable change of volume nd contributes to β_0^r; whereas the subsequent step $[R^{++}SO_4^{--}] \rightleftharpoons R^{++} + SO_4^{--}$ is accompanied with no change of volume and, hence, does not contribute to β_0^r.

So, whereas $$\frac{\mu_m}{c} = \frac{\pi}{1000} \cdot \frac{(\Delta V)^2}{\beta_0^\circ RT} \alpha'(1-\alpha')(1-\alpha);$$

the dissociation constant for the total step is $K = K_{obs}^{(RSO_4)} \times \frac{\alpha'^2}{1-\alpha'}$. With a value of $\alpha' = 0.05$ nearly, along with the observed values of α, it is possible to explain all the results of Kurtze and Tamm (1953); including the values of free energy change from the equation $\Delta F = -RT \log K$. It has been tacitly assumed that the ion pair dissociates just like the neutral molecule. In spite of the many uncertainties involved, this mechanism seems to be responsible for the absorption. The explanation of the second maxima is not possible, unless accurate values of μ_{m_2} and ν_m, are available experimentally.

ACKNOWLEDGMENT

Author's sincere thanks are due to Dr. A. K. Dutta. D.Sc., F.N.I. for the close interest he has shown in the present work.

REFERENCES

Freedmann, 1953, *J. Chem. Phys.*, **21**, 1784.
Kurtze and Tamm, 1953, *Acoustica*, **33**, 3.
Wicke and Eigen, 1952, *Naturwiss*, **39**, 545.